

Heavy Metal Uptake by Herbs. IV. Influence of Soil pH on the Content of Heavy Metals in *Valeriana officinalis* L.

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Abstract The aim of the study was to estimate the influence of soil pH on the uptake of copper, zinc, and manganese by *Valeriana officinalis*. Preliminary studies involved soil analyses to determine acidity, organic matter content, and copper, zinc, and manganese total and bioavailable forms. The study involved atomic absorption spectrometry to determine the concentration of the elements, and mineral soil of pH=5.1 was used in the study, as being typical for central Poland. The copper, zinc, and manganese contents were determined in plants grown in soils which had been modified to cover a wide range of pH values 3–13. The intensity of germination was strongly pH dependent with the highest yield obtained in original, unmodified soil. Surprisingly, high soil alkalinity stimulated copper and manganese uptake while at the same time resulting in a decrease in zinc content.

Keywords *Valeriana officinalis* · Soil · Heavy metals · Herbs · FAAS

Parts I, II, III: Adamczyk (2006), Adamczyk (2007), Adamczyk and Jankiewicz (2008), respectively.

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1 Introduction

Herbs, which have always been the principal form of medicine in developing countries, are once again becoming popular throughout the world, in developing and developed countries alike, with statistics showing that a growing number of people in Europe, North America, and Australia are consulting professional herbalists (Cordell and Colvard 2012; Kumar 2006).

In recent years, much research has been aimed at drugs of plant origin. The World Health Organization estimates that 80 % of the world's population relies on herbal medicine (Cass 2004). In particular, herbal therapies are commonly used for treatment of chronic symptoms of sleep disturbances (Taibi et al. 2007), as this common syndrome affects an ever increasing proportion of the human population. For example, almost one third of all adults in the USA report various symptoms of insomnia (Aikens and Rouse 2005; Barnes et al. 2008; Grewal and Doghramji 2010).

Valeriana officinalis L. (valerian) is a perennial herbaceous plant (Valerianaceae family) that has been widely used in therapy since ancient times and is nowadays widely distributed and cultivated across Europe and Asia, as native there. In Poland, it is one of the major herbs processed by the pharmaceutical industry, with a total annual harvest exceeding 1000 t (Baj 2010).

Valerian root extract demonstrates strong sedative properties, and in the USA and many European countries including Poland, it is used to alleviate states of excessive nervous agitation, anxiety, difficulty with concentration, or insomnia (Bent et al. 2006; Sudati et al. 2009; Weeks 2009). In particular, the valeric acid present in *V. officinalis* exhibits spasmolytic action and reduces tension in gastrointestinal smooth muscles

(Wielgosz et al. 2012). The health properties of valerian are fairly well documented (Ghedira et al. 2008; Patocka and Jakl 2010). The major active compounds are essential oil, valepotriates, and valeric acids with derivatives, although the detailed mechanism of their action is not yet fully understood (Baranauskiene 2007). This situation has prompted studies in biology and medicine of the valerian plant accompanied by identification of its active chemical substances (Erns 2006; Ozkol et al. 2011; Stef et al. 2010; Sudati et al. 2009; Wang et al. 2011). Experimental cultivation conditions as described in the present paper were based on a general knowledge of the *V. officinalis* biology. It is well recognized that this herb prefers moist woodlands and is often planted on a low lying damp sandy humus with possible addition of lime fertilizer (Patocka and Jakl 2010; Bernath 1997).

It is well documented that different conditions of valerian cultivation may cause substantial changes in the chemical constitution of the plant as well as in its medical effects (Tabatabaei 2008). The latter may be also affected by the processing method and storage conditions of the herbs harvested (Kemper 1999; Peirce 1999). In the case of medical products, it is particularly important to control the content of heavy metals accumulated during the plant's growth (WHO 2007; Leśniewicz et al. 2006; Bu et al. 2013). Herbs cultivated on soils with high content of heavy metals often show plant stress symptoms (Ovečka and Takáč 2014; Viehweger 2014) and subsequent variations in plant constituents. This may obviously influence the medical value of particular species. European and Polish domestic regulations are restricted to cadmium, lead, and chromium (WHO 2007; Pharnieuropa 2008; Regulation of the Minister of Health 2003) only. However, many other heavy metals also introduce plant stress, among which zinc, manganese, and copper are the most important (Cheng 2003; Farrag et al. 2012).

Due to the varied bioavailability of heavy metals in soil, their concentration in herbs available on the market may vary significantly (Kalny et al. 2007; Kandziora-Ciupa et al. 2013). Heavy metal uptake by plants is a complex soil-plant process, influenced by many factors such as plant species, genotype, availability, and mobility of metals in soil, soil properties, and all the biogeochemical processes and the microbial activity, at the rhizosphere level, which influence metal mobility and availability to plants (Gębski 1998; Kabata-Pendias and Pendias 1999; Radanovic et al. 2002; Sady and Smoleń 2004; Farrag et al. 2012; Nadgórska-Socha et al. 2013).

The latter were studied in detail, and there is a common understanding reported in the literature that soil pH is the major factor influencing the mobility and bioavailability of heavy metals to plants (Cheng 2003; Domańska and Filipek 2011; Ginocchio et al. 2002; Kukier et al. 2004; Piśkuła and Stepień 2007; Wang et al. 2006). Generally, the mobility of metals in alkaline soils decreases in the order $Cd > Ni > Zn > Mn > Cu > Pb$ (Fijałkowski et al. 2012) and is highly variable and strongly dependent on the content and type of organic ingredients as present in the soil (Badaway et al. 2002; Brailier et al. 1996; du Laing et al. 2008; Wang et al. 2006). In particular, soils with pH values below 7 are very prone to heavy metal migration from soil solid components into the soil solution, as has been observed for copper (Wang et al. 2006; Zeng et al. 2011), manganese (Alam et al. 1999), and zinc (Bang and Hesterberly 2004; Marschner 1993).

Herbal therapies are usually long term. Therefore, even small heavy metal doses as present in particular plant may accumulate in patient body over a long period of time (Aikens and Rouse 2005; Kraft and Hobbs 2004).

In this paper, the influence of soil pH on the uptake of selected heavy metals by valerian plants cultivated in the model pot experiments was investigated. This work follows our ongoing investigations on the influence of cultivation conditions and methods on the heavy metal uptake by herbs (Adamczyk 2006; Adamczyk 2007; Adamczyk and Jankiewicz 2008).

2 Materials and Methods

Soil samples were collected in October 2011, in Krokocice village (Szadek municipality, Łódź province,

Table 1 Results of soil analysis

Analysis	Results	
Soil pH	5.1	
Organic matter	3.33 %	
Metal content	Total (mg/kg)	Bioavailable (mg/kg)
	Copper	
	4.40±0.44	1.23±0.16
	Zinc	
	23.3±1.9	3.63±0.41
Manganese		
	253±15	83.6±1.5

$n=4$; $p=95\%$ (n , number of sample; p , confidence level)

Table 2 The content of Cu, Zn, and Mn in the certified reference material

Metal	Certified value (mg/kg)	Found (mg/kg)	Recovery (%)
Copper	7.77±0.53	6.93±0.38	89
Zinc	33.5±2.1	34.5±0.9	103
Manganese	191±12	179±9	94

$n=4$; $p=95\%$ (n , number of samples; p , level of confidence)

about 30 km from Łódź, Poland), on agricultural land located away from excessive traffic according to the procedure in PN-ISO 10381-4:2007. The samples were subsequently dried in a well-ventilated place, sifted through a 2-mm stainless steel sieve, and finally stored in plastic bags. Soil pH was measured by the potentiometric method in 1 mol/dm³ potassium chloride solution (PN-ISO 10390:1997). The well-established gravimetric method for the determination of soil organic matter by the mass loss at 550 °C was applied (Nelson and Sommers 1996; ASTM 2000; Schumacher 2002). The bioavailable forms of metals were determined in 1 mol/dm³ hydrochloric acid extracts (PN-ISO 11259:2001). The total metal content was measured in samples mineralized using the Anton Paar Multiwave 3000 closed system instrument. The mixture of concentrated HNO₃ (6 cm³) and HCl (2 cm³) was applied (0.5 g of soil). Metal concentrations were measured by FAAS with the GBC 932 plus spectrometer. The results are summarized in Table 1.

2.1 Soil pH Adjustment and Preparation of Plant Samples

Soil pH was originally adjusted to four values: 3.5, 4.1, 10, and 13. Samples of agricultural soil (500 g) were placed in 16 plastic pots (4 for each pH value), and then appropriate amounts of 0.5 mol/l H₂SO₄ (30 or 125 ml)

or CaO (8 or 16 g) were added to each sample and carefully mixed manually. The soil with additives prepared in this way was subsequently air-dried and subjected to pH measurements. The whole procedure was consequently repeated until the final pH value was established. For the plant growth, 40 plastic pots were used (4 for each pH value and 4 extra representing additive-free soil).

The weight of soil sample used per pot was the same as in the pH adjustment (500 g). Seeds of *V. officinalis* (from P.H. Legutko company, Poland) were sown in an amount of 0.2 g (approximately 200 seeds) per pot. All pots were kept in a greenhouse at a controlled temperature of 23±2 °C. All plants were regularly watered by deionized water and soil moisture was kept at 60 % of its maximal water holding capacity. The *V. officinalis* was harvested 3 months after they were sown. After harvesting, the plants were washed several times in deionized water and oven-dried at 45 °C to a constant weight. The dried valerian plant roots and seeds were subjected to a microwave mineralization process under concentrated HNO₃ (6 cm³) and HCl (1 cm³) (0.5-g sample). The zinc, manganese, and copper concentrations in the resulting solutions were determined by FAAS with the GBC 932 plus spectrometer.

The accuracy of the method applied was controlled by parallel analysis of the certified reference material INCT-MPH-2, containing a mixture of selected Polish herbs. Results are collected in Table 2. Data were statistically evaluated using a one-way ANOVA as implemented in the Microsoft Excel 2010.

3 Results

The results of the soil analysis and metal bioavailability are summarized in Table 1. The organic matter content

Table 3 Selected metal content accompanied by average dry plant weights and germination rates as determined for *Valeriana Officinalis*

Cultivation conditions	Germination rate (%)	Average dry plant weight ^a (g)	Average dry roots weight ^b (g)	Metals content in roots (mg/kg)		
				Copper	Zinc	Manganese
pH=5.1	34	1.68±0.42	0.62±0.32	8.50±1.20	49.5±4.1	81.0±2.1
pH=10	11	0.40±0.17	0.26±0.11	15.0±1.5	26.2±1.7	106±2

^a Average dry plant weight as calculated for a single plant (g)

^b Average dry root weight as calculated for a single plant (g)

Table 4 ANOVA parameters for metal content in *Valeriana officinalis* across two soil pH values

Source of variation	SS	MS	F	P value	Test F
Zinc	1092.781	1092.781	109.0283	$4.52 \cdot 10^{-5}$	13.745
Copper	84.43501	84.43501	52.62893	0.000349	13.745
Manganese	1225.125	1225.125	230.7928	$5.13 \cdot 10^{-6}$	13.745

was determined as 3.33 %, which indicates the mineral character of the soil (Fotyma and Mercik 2003; Dobrzański and Zawadzki 1995), while the low copper, zinc, and manganese content clearly indicates that, according to the generally accepted international standards (Council Directive 86/278/EEC 1986; IUSS Working Group WRB 2006), the soil is not contaminated by these metals. The results for the metal content in the valerian roots and seeds are summarized in Table 3. Results of ANOVA clearly showed that variations of metal contents as calculated for herbs grown in soils of pH values 5.1 and 10.0 are significantly different (Table 4).

The most intensive germination and plant growth was observed at pH=5.1. Increased alkalinity to pH=10 significantly inhibited both the seed germination and the plant growth (Fig. 1). Despite several attempts, valerian seeds inoculated in soil characterized by a low or a very high pH values (3.5, 4.1, 13.0) failed to germinate. Metal content in seeds was 11.5 ± 1.5 , 37.2 ± 0.6 , and 63.6 ± 2.2 mg/kg for copper, zinc, and manganese, respectively.

4 Discussion

It has been widely documented that heavy metal uptake by plants from soil is strongly pH dependent (Bolan et al. 2003; Chairidchai and Ritchie 1993; Hollier and Reid 2005; Wang et al. 2006), and this conclusion was further confirmed by the present paper. Increasing the soil pH to 10 resulted in a significant decrease in the zinc content of all plants investigated (Table 3). This is quite consistent with numerous literature data, which indicate that at high soil alkalinity, plants are not prone to zinc uptake (Bang and Hesterberg 2004; Kukier et al. 2004; Radanovic et al. 2002; Sukreeyapongse et al. 2002; Tyler and Olsson 2001; Wang et al. 2006; Zeng et al. 2011). Valerian seeds did not germinate in the soil of pH value below 4.5; therefore, it was not possible to determine the metal uptake in these extremely acidic conditions. However, there is a general understanding that low pH prompts high metal mobility (Reddy et al. 1995; Landner and Reuther 2005; Violante et al. 2010). In particular, Piłkuła and Stepień (2007) pointed out that the significant

Fig. 1 Plants cultivated on soil with pH=5.1 and pH=10 after harvest

zinc bioavailability in acidic conditions may be related to the formation of soluble mineral entities further releasing metal ions into the soil environment. Surprisingly, copper and manganese contents in herbs grown in highly alkaline soil (pH=10) are significantly higher as compared to plants cultivated in medium acidic conditions (pH=5.1). Increasing the soil pH does not necessarily reduce the amount of bioavailable heavy metals (Wu et al. 2011). According to Kabata-Pendias and Pendias (1999), mobility of these metals in alkaline soils is often increased due to the formation of complexes involving the soil organic entities which are available for plants (Gębski 1998; Majewska and Kurek 2002). It is quite well documented that pH and the redox conditions influence manganese bioavailability in soils (Marschner 1995; Porter et al. 2004). In acidic soils (pH<5.5) additionally characterized by high redox potential (Kogelmann and Sharpe 2006), manganese oxides are easily reduced to Mn^{2+} ions which are available for plants (Adriano 2001; Watmough et al. 2007). At high soil pH (pH>8.0), chemical Mn^{2+} auto-oxidation may lead to the formation of MnO_2 , Mn_2O_3 , Mn_3O_4 , or even Mn_2O_7 , which are not easily accessible to plants (Ducic and Polle 2005; Gherardi and Rengel 2004; Humpries et al 2007). Furthermore, these oxides can readily absorb on soil particles, further decreasing the manganese bioavailability (Fageria et al. 2002).

On the contrary, several reports have suggested that available forms of manganese may be produced under reduced conditions, even at high soil pH values (Hue 1988). In a similar way to the experimental setup as presented in this paper, a reducing environment existed when an excess of water in soil was combined with good availability of organic matter (El-Jaoual and Cox 1998). The latter interacted with solid manganese oxides transforming them into soluble complexes easily available for plants (Millaleo et al. 2010). It is also quite well documented that increasing pH, induced by lime, intensifies microbiological processes in soil (Fuentes et al. 2006; Weyman-Kaczmarkowa and Pedziwilk 1999c). Weyman-Kaczmarkowa and Pedziwilk (2000) have reported that lime alkalization prompts bacterial growth, especially in loose sandy or sandy loam soils. The resulting increase in microbial biomass concentration accumulated considerable amounts of heavy metals (Bergman et al. 1999; Bewley and Stotzky 1983; Peick et al. 1999). The latter mechanism is presumably responsible for the high manganese and copper uptake by valerian plants as observed in the present study.

Our future research will concentrate on detailed mechanism of heavy metal uptake by *V. officinalis* cultivated in variable soil environments relative to the growing importance of herb production for the domestic and regional economics.

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References

- Adamczyk, D. (2006). The effect of thiuram on the uptake of lead and copper by *Melissa officinalis*. *Environmental Engineering Science*, 23(4), 610–614.
- Adamczyk, D. (2007). The effect of thiuram on the uptake of zinc by *Melissa Officinalis*. *Ecology Chemistry and Engineering*, 14(8), 781–787.
- Adamczyk, D., & Jankiewicz, B. (2008). Effect of thiuram on uptake of copper, zinc and manganese by *Valeriana Officinalis* L. *Polish Journal of Environmental Studies*, 17(5), 823–826.
- Adriano, D. C. (2001). *Trace elements in terrestrial environments. Biogeochemistry, bioavailability and risks of metals* (p. 867). New York: Springer-Verlag.
- Aikens, J. E., & Rouse, M. E. (2005). Help-Seeking for Insomnia among adult patients in primary care. *Journal of the American Board of Family Medicine*, 18(4), 257–261.
- Alam, S. M., Naqvi, S. S., & Ansari, M. R. (1999). Impact of soil pH on nutrient uptake by crop plants. In M. Pessarakli (Ed.), *Handbook of Plant and Crop Stress* (pp. 51–60). New York: Marcel Dekker.
- ASTM (2000) Standard test methods for moisture, ash, and organic matter of peat and other organic soils. Method D 2974-00. American Society for Testing and Materials. West Conshohocken, PA.
- Badaway, S. H., Helal, M., Chaudri, A., Lawlor, K., & McGrath, S. (2002). Soil solid phase controls lead activity in soil solution. *Journal of Environmental Quality*, 31, 162–167.
- Baj, T. (2010). Valerian in sleep disorders. *Apothecary Polish*. Scripture of the Supreme Chamber of Pharmacists 42/20.
- Bang, J., & Hesterberg, D. (2004). Dissolution of trace element contaminants from two coastal plain soils as affected by pH. *Journal of Environmental Quality*, 33, 891–901.
- Baranauskiene, R. (2007). Essential oil composition of *Valeriana officinalis* SSP. *Officinalis* grown in Lithuania. *Chemistry of Natural Compounds*, 43(3), 331–333.
- Barnes, P. M., Bloom, B., & Nahin, R. L. (2008). Complementary and alternative medicine use among adults and children: United States 2007. *National Health Statistics Report*, 12(10), 1–24.
- Bent, S., Padula, A., Moore, D., Patterson, M., & Mehling, W. (2006). Valerian for sleep: a systematic review and meta-analysis. *American Journal of Medicine*, 119, 1005–1012.
- Bergman, I., Lundberg, P., & Nilsson, M. (1999). Microbial carbon mineralization in an acid surface peat: effects of environmental factors in laboratory incubations. *Soil Biology and Biochemistry*, 31, 1867–1877.

- Bernath, J. (1997). Cultivation of Valerian; Valerian: the genus *Valeriana* ed. by Houghton 77-101.
- Bewley, R. J. F., & Stotzky, G. (1983). Simulated acid rain (H_2SO_4) and microbial activity in soil. *Soil Biology and Biochemistry*, 4, 425–429.
- Bolan, N., Adriano, D., & Curtin, D. (2003). Soil acidification and liming interactions with nutrient and heavy metal transformation and bioavailability. *Advances in Agronomy*, 78, 215–272.
- Braillier, S., Harrison, R. B., Henny, C. L., & Dogsen, X. (1996). Liming effects on availability of Cd, Cu, Ni and Zn in a soil amended with sewage sludge 16 years previously. *Water, Air and Soil Pollution*, 86, 195–206.
- Bu, K., Cizdziel, J. V., & Reidy, L. (2013). Analysis of herbal supplements for selected dietary minerals and trace elements by laser ablation-and solution-based ICPMS. *Microchemical Journal*, 106, 244–249.
- Cass, H. (2004). Herbs for the nervous system: ginko, kava, valerian, passionflower. *Seminars Integrated Medicine*, 2, 82–88.
- Chairidchai, P., & Ritchie, G. S. P. (1993). Effect of citrate and pH on zinc uptake by wheat. *Agronomy Journal*, 85, 322.
- Cheng, S. (2003). Effect of heavy metals on plants and resistance mechanisms. *Environmental Science and Pollution Research*, 10(4), 256–264.
- Cordell, G. A., & Colvard, M. D. (2012). Natural products and traditional medicine: turning on a paradigm. *Journal of Natural Products*, 75, 514–525.
- Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Official Journal L 181:6–12.
- Dobrzański, B., Zawadzki, S. (1995). Soil Science, PWRL Warsaw
- Domańska, J., & Filipek, T. (2011). Zinc accumulation in cooksfoot in dependence on kind of soil pH, and Cd or Pb soil contamination. *Environmental and Natural Resources*, 48, 67–73.
- du Laing, G., de Vos, R., Vandecasteele, B., Lesage, E., Tack, F. M. G., & Verloo, M. G. (2008). Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary. *Estuarine, Coastal and Shelf Science*, 77, 589–602.
- Ducic, T., & Polle, A. (2005). Transport and detoxification of manganese and copper in plants. *Brazilian Journal of Plant Physiology*, 17, 103–112.
- El-Jaoual, T., & Cox, D. (1998). Manganese toxicity in plants. *Journal of Plant Nutrition*, 21, 353–386.
- Ernst, E. (2006). Herbal remedies for anxiety-a systematic review of controlled clinical trials. *Phytomedicine*, 13(3), 205–208.
- Fageria, N., Baligar, V., & Clark, R. (2002). Micronutrients in crop production. *Advances in Agronomy*, 77, 185–268.
- Farrag, K., Senesi, N., Nigro, F., Petrozza, A., Palma, A., Shaarawi, S., & Brunetti, G. (2012). Growth responses of crop and weed species to heavy metals in pot and field experiments. *Environmental Science and Pollution Research*, 19, 3636–3644.
- Fijałkowski, K., Kacprzak, M., Grobelak, M., & Placek, A. (2012). The influence of selected soil parameters on the mobility of heavy metals in soils. *Engineering and Environmental Protection*, 15(1), 81–92.
- Fotyma, M., Mercik, S. (2003). Agricultural Chemistry, PWRL Warsaw
- Fuentes, J. P., Bezdicsek, D. F., Flury, M., Albrecht, S., & Smith, J. L. (2006). Microbial activity affected by lime in a long-term no-till soil. *Soil and Tillage Research*, 88, 123–131.
- Gębski, M. (1998). Soil factors and fertilizer affecting the uptake of heavy metals by plants. *Advances in Agricultural Sciences*, 5(3), 16.
- Ghedira, K., Goetz, P., & Len, J. R. (2008). *Valeriana officinalis* L. *Phytothérapie*, 6, 253–257.
- Gherardi, M., & Rengel, Z. (2004). The effect of manganese supply on exudation of carboxylates by roots of lucerne (*Medicago sativa*). *Plant and Soil*, 260, 271–282.
- Ginocchio, R., Rodriguez, P. H., Badilla-Ohlbaum, R., Allen, H. E., & Lagos, G. E. (2002). Effect of soil copper content and pH on copper uptake of selected vegetables grown under controlled conditions. *Environmental Toxicology and Chemistry*, 21(8), 1736–44.
- Grewal, R., & Doghramji, K. (2010). *Epidemiology of Insomnia, Clinical Handbook of Insomnia, Current Clinical Neurology*, 13-22 Edit. Attarian and Schuman: Springer Science+ Business Media.
- Hollier, C., Reid, M. (2005). Agriculture notes, Acid Soils. April. AG1182. ISSN: 1329-8062
- Hue, N. (1988). A possible mechanism for manganese toxicity in Hawaii soils amended with a low-Mn sewage sludge. *Journal of Environmental Quality*, 17, 473–479.
- Humphries, J., Stangoulis, J., & Graham, R. (2007). Manganese. In A. Barker & D. Pilbeam (Eds.), *Handbook of Plant Nutrition* (pp. 351–366). USA: Taylor and Francis.
- IUSS Working Group WRB (2006) World Reference Base for Soil Resources 2006. World Soil Resources Reports No. 103. (FAO: Rome).
- Kabata-Pendias, A., Pendias, H. (1999). Biogeochemistry of Trace Elements. Edit. II PWN.
- Kalny, P., Fijałek, Z., Daszczyk, A., & Ostapczuk, P. (2007). Determination of selected microelements in polish herbs and their infusions. *The Science of the Total Environment*, 381, 99–104.
- Kandziora-Ciupa, M., Ciepał, R., Nadgórska-Socha, A., & Barczyk, G. (2013). A comparative study of heavy metal accumulation and antioxidant responses in *Vaccinium myrtillus* L. leaves in polluted and non-polluted areas. *Environmental Science and Pollution Research*, 20, 4920–4932.
- Kemper, K.J. (1999). Valerian (*Valeriana officinalis*), The Longwood Herbal Task Force (<http://www.mcp.edu/herbal/default.htm>) and The Center for Holistic Pediatric Education and Research (<http://www.childrenshospital.org/holistic/>) 1-25.
- Kogelmann, W., & Sharpe, W. (2006). Soil acidity and manganese in declining and nondeclining sugar maple stands in Pennsylvania. *Journal of Environmental Quality*, 35, 433–441.
- Kraft, K., Hobbs, Ch. (2004). Pocket Guide to Herbal Medicine, Thieme, 125.
- Kukier, U., Peters, C. A., Chaney, R. L., Angle, J. S., & Roseberg, R. J. (2004). The effect of pH on metal accumulation in two *Alyssum* species. *Journal of Environmental Quality*, 33(6), 2090–2102.
- Kumar, V. (2006). Potential medicinal plants for CNS disorders: an overview. *Phytotherapy Research*, 20, 1023–1035.
- Lander, L., & Reuther, R. (2005). Metals in society and in the environment. A critical review of current knowledge on

- fluxes, speciation, bioavailability and risk for adverse effects of copper, chromium, nickel and zinc. *Environmental Pollution*, 8, 139–274.
- Leśniewicz, A., Jaworska, K., & Zymicki, W. (2006). Macro- and micronutrients and their bioavailability in polish herbal medicaments. *Food Chemistry*, 99, 670–679.
- Majewska, M., & Kurek, E. (2002). Microorganisms - factor that modifies the concentration of cadmium in the soil solution. *Advances in Agricultural Science*, 1(3), 13.
- Marschner, H. (1993). Zinc uptake from soils, zinc in soils and plants. *Developments in Plant and Soils Science by editor: Robson AD*, 55, 59–77.
- Marschner, H. (1995). *Mineral Nutrition of Higher Plants* (2nd ed.). San Diego C: Academic Press. 889.
- Millaleo, R., Reyes-Diaz, M., Ivanov, A. G., Mora, M. L., & Alberdi, M. (2010). Manganese as essential and toxic element for plants: transport, accumulation and resistance mechanisms. *Journal of Soil Science Plant Nutrition*, 10(4), 470–481.
- Nadgórska-Socha, A., Kafel, A., Kandziora-Ciupa, Gospodarek, J., & Zawisza-Raszka, A. (2013). Accumulation of heavy metals and antioxidant responses in *Vicia faba* plants grown on monometallic contaminated soil. *Environmental Science and Pollution Research*, 20, 1124–1134.
- Nelson, D.W., Sommers, L.E. (1996) Total carbon, organic carbon, and organic matter. In: Methods of Soil Analysis, Part 2, 2nd ed., A.L. Page et al., Ed. Agronomy Am Soc Agron, Inc Madison, WI 9:961-1010.
- Ovečka, M., & Takáč, T. (2014). Managing heavy metal toxicity stress in plants: biological and biotechnological tools. *Biotechnology Advances*, 32(1), 73–86.
- Ozkol, H., Koyuncu, I., & Tuluze, Y. (2011). Some medicinal plants counteract alterations of neuroendocrine stress response system, oxidative and nitrosative stress caused by repeated restraint in rats. *Journal of Medicinal Plant Research: Planta Medica*, 5(17), 4360–4368.
- Patočka, J., & Jakl, J. (2010). Biomedically relevant chemical constituents of *Valeriana officinalis*. *Journal of Applied Biomedicine*, 8, 11–18.
- Peick, B., Graumann, P., Schmid, R., Marahiel, M., & Werner, D. (1999). Differential pH induced proteins in *Rhizobium tropici* CIAT 899 and *Rhizobium etli* CIAT 611. *Soil Biology and Biochemistry*, 31, 189–194.
- Peirce, A. (1999). *The American Pharmaceutical Association practical guide to natural medicines*. New York: William Morrow and Company, Inc.
- Pharmeuropa, Herbal drugs (2008); 20(2).
- Pikuła, D., & Stępień, W. (2007). Effect of soil pH on the uptake of heavy metals by plants. *Fragmentation Agronomy*, 2(94), 227–237.
- PN-ISO 10381-4. (2007). Soil quality - Sampling - Part 4: rules for procedure during the research areas of natural, semi-natural and cultivated.
- PN-ISO 10390. (1997). Agricultural chemical analysis of the soil. Determination of pH.
- PN-ISO 11259. (2001). Soil quality - A simplified description of the soil.
- Porter, G., Bajita-Locke, J., Hue, N., & Strand, S. (2004). Manganese solubility and phytotoxicity affected by soil moisture, oxygen levels, and green manure additions. *Communications in Soil Science and Plant Analysis*, 35, 99–116.
- Radanovic, D., Antic-Mladenovic, S., & Jakovljevic, M. (2002). Influence of Some Soil Characteristics on Heavy Metal Content in *Hypericum perforatum* L. and *Achillea millefolium* L. *Acta Horticulture (ISHS)*, 576, 295–301.
- Reddy, K. J., Wan, L., & Gloss, S. P. (1995). Solubility and mobility of copper, zinc and lead in acidic environments. *Plant and Soil*, 171, 53–58.
- Regulation of the Minister of Health 13.01.2003 on maximum levels of chemical and biological contaminants that may be present in food, food ingredients, allowed additional substances, substances or processing aids on food Dz.U. 37, 326.
- Sady, W., Smoleń, S. (2004). Influence factors soil-fertilizer the accumulation of heavy metals in plants. National Symposium “Effectiveness of the use of fertilizers the horticultural crops”, Krakow.
- Schumacher, B.A. (2002). Methods for the determination of total organic carbon (toc) in soils and sediments, United States Environmental Protection Agency Environmental Sciences Division National Exposure Research Laboratory, Las Vegas.
- Stef, D. S., Gergen, I., Trasca, T. I., Hărmănescu, M., Stef, L., Drugă, M., Biron, R., & Hegheduş- Mindru, G. (2010). Screening of 33 medicinal plants for the microelements content. *Journal of Animal Science and Biotechnology*, 43(1), 127–132.
- Sudati, H. J., Fachinetto, R., Pereira, R. P., Boligon, A. A., Athayde, M. L., Soares, F. A., de Vargas Barbosa, N. B., & Rocha, J. B. T. (2009). In vitro antioxidant activity of *Valeriana officinalis* against different neurotoxic agents. *Neurochemical Research*, 34, 1372–1379.
- Sukreeyapongse, O., Holme, P. E., Strobel, B. W., Panichsakpatana, S., Magid, J., & Hansen, H. C. B. (2002). pH dependent release of cadmium, copper and lead from natural and sludge amended soils. *Journal of Environmental Quality*, 31, 1901–1909.
- Tabatabaei, S. J. (2008). Effects of cultivation systems on the growth, and essential oil content and composition of valerian. *Journal of Herbs, Spices and Medicinal Plants*, 14(1–2), 54–67.
- Taibi, D. M., Landis, C. A., Petry, H. V., & Vitiello, M. (2007). A systematic review of valerian as a sleep aid: safe but not effective. *Sleep Medicine Reviews*, 11, 209–230.
- Tyler, G., & Olsson, T. (2001). Concentrations of 60 elements in the soil solution as related to the soil acidity. *European Journal of Soil Science*, 52, 151–165.
- Viehweger, K. (2014). How plants cope with heavy metals. *Botanical Studies*, 55, 35.
- Violantel, A., Cozzolino, V., Perelomov, L., Caporale, A. G., & Pigna, M. (2010). Mobility and bioavailability of heavy metals and metalloids in soil environments. *Journal of Soil Science Plant Nutrition*, 10(3), 268–292.
- Wang, A. S., Angle, J. S., Chaney, R. L., Delorme, T. A., & Reeves, R. D. (2006). Soil pH effects on uptake of Cd and Zn by *Thlaspi caerulescens*. *Plant and Soil*, 281, 325–337.
- Wang, P. C., Ran, X. H., Chen, R., Luo, H. R., Ma, Q. Y., Liu, Y. Q., et al. (2011). Sesquiterpenoids and Lignans from the Roots of *Valeriana officinalis* L. *Chemistry & Biodiversity* 8, 1908–1913.
- Watmough, S., Eimer, M., & Dillon, P. (2007). Manganese cycling in central Ontario forests: response to soil acidification. *Applied Geochemistry*, 22, 1241–1247.

- Weeks, B. S. (2009). Formulations of dietary supplements and herbal extracts for relaxation and anxiolytic action: RelarianTM. *Medical Science Monitor*, 15(11), 256–262.
- Weyman-Kaczmarkowa, W., & Pedziwilk, Z. (2000). The development of fungi as affected by pH and type of soil, in relation to the occurrence of bacteria and soil fungistatic activity. *Microbiol Research*, 155(2), 107–112.
- Weyman-Kaczmarkowa, W., & Pedziwilk, Z. (1999). The development of actinomycetes and fungistatic activity of soils as affected by pH and soil type. *Acta Microbiology Polonica*, 1, 85–92.
- WHO guidelines for assessing quality of herbal medicines with reference to contaminants and residues, WHO Library Cataloguing-in-Publication Data, 2007.
- Wielgosz, T., Kozłowski, J., Cis, J. (2012). Herbs from the pharmacy of nature. Publicat.
- Wu, D., Liu, Y., Liu, Y., Dong, y., Chen, J., Feng, y., Du, J. (2011). Study on Available Copper Content in Cultivated Soils and its Affecting factors in Zhuhai. International Conference on Computer Distributed Control and Intelligent Environmental monitoring, 1350-1353.
- Zeng, F., Ali, S., Zhang, H., Ouyang, Y., Qiu, B., Wu, F., & Zhang, G. (2011). The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. *Environmental Pollution*, 159, 84–91.